Surface Plasmon Assisted Kondo Resonances on a Metallic Nanowire

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In this letter we propose an experiment to measure the Kondo effect for magnetic atoms adsorbed on the surface of a metallic nanowire. In addition to the traditional *sp-d* hybridization, by introducing the strong electromagnetic field of the localized surface plasmon on the nanowire, we show that it is possible to observe additional *sp-d* electron transfer processes assisted by surface plasmons. Due to the good surface-to-volume ratio of the nanowire, the Kondo resonances here would be revealed as multiple anti-resonances in the differential conductance versus bias voltage curve.

The Anderson model was introduced initially to explain the localized magnetic moments in metals[1]. The Coulomb repulsion on the impurities for localized orbitals provides a great variety of interesting physics. One of the important features is the appearance of the Kondo resonance near the Fermi surface. It leads to many unusual effects particularly in strongly correlated electronic systems. More recently the scanning tunneling microscopy measurement of a single magnetic atom on a metallic surface[2] was a direct observation of Kondo resonance.

Meanwhile, *surface plasmon resonance* (SPR), which has been known for a long time to give rise to various colors in fine noble metal particles, is an effect that can be understood in classical electromagnetic theory[3, 4]. Its amplitude of EM field is strongly enhanced due to the fact that it is highly localized near metal surfaces. Also depending on the geometry, surface plasmon can be non-radiative in some cases and therefore travel a long distance.[5] These special characteristics have allowed SPR to find its ways to many applications in different areas, such as surface enhanced Raman scattering[6].

In this letter we propose an experiment as illustrated in Fig. 1. The use of metallic nanowire serves two purposes here. One is to maximize the scattering of the electrons by the surface of the wire, so that the electrons going through the wire are more sensitive to the Kondo atoms on the surface. The other is for introducing surface plasmons. Since surface plasmons only exist near the surface, the localization of the EM field caused by the confinement in the transverse directions can ensure the large EM enhancement. The strong EM field couples to electrons through the $\mathbf{j}\cdot\mathbf{A}$ interaction. The excitation of the surface plasmon can be carried out in one of the electrodes. It has been shown that surface plasmon can travel coherently up to 10 μm in a single-crystalline silver nanowire[8].

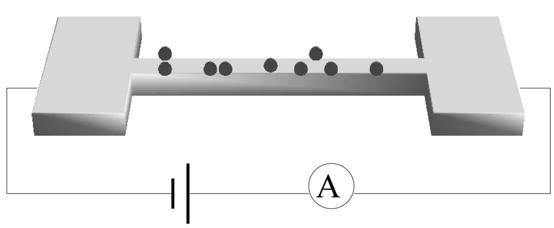

FIG. 1: Illustration of the experimental setup. T he suspended metal nanowire is connected to an electrode at each end for the measurement of the conductance. The Kondo atoms such as Co are chemically adsorbed on the wire. The surface plasmon can be excited by shining laser on one of the electrodes[7].

The Hamiltonian considered is

$$\begin{aligned} H &= H_C + H_T; \\ H_C &= \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} + \epsilon_d \sum_{i=1}^{n} \sum_{\nu=1}^{N_d} d^\dagger_{i\nu} d_{i\nu} + U \sum_{i\nu\nu'} n_{id\nu} n_{id\nu'} \\ &\quad + \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} a^\dagger_{\mathbf{q}} a_{\mathbf{q}} + \sum_{\mathbf{k}\sigma i\nu\mathbf{q}} V_{\mathbf{k}i\mathbf{q}} c_{\mathbf{k}\sigma} d^\dagger_{i\nu} (a_{\mathbf{q}} + a^\dagger_{\mathbf{q}}) + \text{hc}, \\ H_T &= \sum_{j=L,R} \sum_{\mathbf{k}\sigma} (\epsilon_{\mathbf{k}} + \mu_j) b^\dagger_{j\mathbf{k}\sigma} b_{j\mathbf{k}\sigma} \\ &\quad + \sum_{j=L,R} \sum_{\mathbf{k}\mathbf{k}'\sigma} t_{j\mathbf{k}\mathbf{k}'} c_{\mathbf{k}\sigma} b^\dagger_{j\mathbf{k}'\sigma} + \text{hc}. \end{aligned} \tag{1}$$

H_C describes the Anderson model for a nanowire with n impurities coupled to assisting photons. $c_{\mathbf{k}\sigma}$ and $d_{i\nu}$ are the annihilation operators for the electrons on the wire and on the ith atom. $a_{\mathbf{q}}$ is the annihilation operator for the surface plasmon. The indices $\mathbf{k}$ and $\mathbf{q}$ are assumed continuous in the longitudinal direction and discrete in the transverse directions of the wire. The inelastic electron-surface plasmon scattering term comes from the $\mathbf{j}\cdot\mathbf{A}$ interaction, where $\mathbf{j}$ is the tunneling current between the wire and the atom. The same $\mathbf{j}\cdot\mathbf{A}$ interaction for the current inside the wire has been integrated into the self-energy of the EM field which gives rise to the negative dielectric constant in metal and forms the surface plasmon[9]. The tunneling term in the original Anderson model for the *sp-d* hybridization is included in the $\mathbf{q}=0$ term, where $\omega_{\mathbf{q}=0}=0$. H_T describes the coupling of the nanowire to the identical electrodes at both ends. $b_{L\mathbf{k}\sigma}$ and $b_{R\mathbf{k}\sigma}$ denote the annihilation operators for the electrons on the left and the right lead, respectively. μ_L and μ_R are the chemical potentials of the fermi seas on the leads.

The surface plasmon field on the nanowire in general has two kinds of modes, leaky modes and bound

modes.[10]. In both cases, the condition for surface plasmon resonance derived from classical Mie scattering theory is $\mathrm{Re}[\varepsilon_m(\omega = \omega_{\mathrm{SPR}})] = -\varepsilon_0$. ε_m is the dielectric constant of the metal, and ε_0 is that of the surrounding medium which is real and positive. The mechanisms for the energy loss in the two kinds of modes are different. The leaky modes lose energy mostly due to irradiation. For the bound modes it is mostly caused by the internal dissipation of the metal characterized by $\mathrm{Im}[\varepsilon_m]$, which classically can be attributed to the Drude damping. However, when the size of the nanostructure is considerably smaller than the electron mean free path, the dissipation of both bound modes and leaky modes is dominated by $\mathrm{Im}[\varepsilon_m]$ as a result of the electrons' scattering with the surface[11]. In either case, the surface plasmon frequency dependence of the field amplitude, or equivalently the electron-surface plasmon coupling constant, can be approximated as

$$V_{\mathbf{k}i\mathbf{q}} \simeq e^{i\mathbf{k}\cdot\mathbf{r}_i} V_{\mathbf{q}} = \left(V \frac{i\kappa/2}{\omega_{\mathbf{q}} - \omega_{\mathrm{SPR}} + i\kappa/2} + V_0 \delta_{\mathbf{q},0} \right) e^{i\mathbf{k}\cdot\mathbf{r}_i}, \tag{2}$$

with κ the full width of the resonance. The electron momentum dependence of the coupling constant enters with different locations of the Kondo atoms. V_0 describes the original *sp*-*d* hybridization between magnetic adatom and the metallic nanowire and V describes the coupling of the *sp*-*d* current with the surface plasmon field. For an isolated gold nanowire of diameters ~ 30 nm and micrometers length, the surface plasmon has a resonance at ~ 525 nm free space wavelength and a full width of ~ 50 nm[12]. The intensity of the local electric field is estimated to exceed the incident field by 10^3[13].

The DC current on the nanowire is given by the Landauer formula in an interacting electron region[14]

$$J = -\frac{2e}{h} \int d\epsilon [f_L(\epsilon) - f_R(\epsilon)] \mathrm{Im}[\mathrm{tr}\{\Gamma G^r\}], \tag{3}$$

where f_L and f_R is the Fermi distribution functions on the left and the right leads, $G^r \equiv G^r_{\mathbf{k}\sigma\mathbf{k}'\sigma'}$ is the full retarded Green's function for the electrons on the wire, and $\Gamma \equiv \Gamma^L \Gamma^R / (\Gamma^L + \Gamma^R)$. Γ^L is the electron tunneling rate to the left lead and is defined as $\Gamma^L_{\mathbf{k}\sigma\mathbf{k}'\sigma} = 2\pi \sum_{\mathbf{k}''} \rho^L_{\mathbf{k}''} t_{\mathbf{k}\mathbf{k}''} t^*_{\mathbf{k}''\mathbf{k}'}$, so is Γ^R. $\rho^L_{\mathbf{k}''}$ is the density of states in the left lead. If we assume that Γ^L and Γ^R are constants, then the expression is simplied to

$$J = -\frac{2e\Gamma}{h} \int d\epsilon [f_L(\epsilon) - f_R(\epsilon)] \sum_{\mathbf{k}\sigma\mathbf{k}'\sigma'} \mathrm{Im}\left[G^r_{\mathbf{k}\sigma\mathbf{k}'\sigma'}(\epsilon)\right]. \tag{4}$$

Here we expand the retarded Green's function to second order

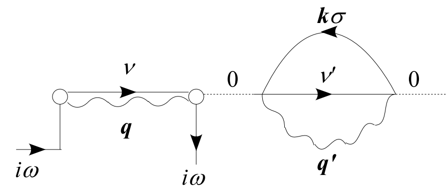

FIG. 2: Lowest non-trivial order Feynman diagram for $F(i\omega)$ in the $1/N$ expansion plotted with the same rules used in Ref.([15]). The self energy correction for the left part of the diagram where there is one localized electron and one more or one less surface plasmon is neglected because of being at least in the order of $(1/N)^1$.

$$\begin{aligned} \sum_{\mathbf{k}\sigma\mathbf{k}'\sigma'} G^r_{\mathbf{k}\sigma\mathbf{k}'\sigma'}(\epsilon) &\simeq \sum_{\mathbf{k}\sigma} G^0_{\mathbf{k}\sigma\mathbf{k}\sigma} \\ &+ \sum_{i=1}^{n} \sum_{\mathbf{k}\sigma\mathbf{k}'\sigma'} G^0_{\mathbf{k}\sigma\mathbf{k}\sigma} e^{i\mathbf{k}\cdot\mathbf{r}_i} F(\epsilon) e^{-i\mathbf{k}'\cdot\mathbf{r}_i} G^0_{\mathbf{k}'\sigma'\mathbf{k}'\sigma'}; \quad (5) \\ G^0_{\mathbf{k}\sigma\mathbf{k}\sigma} &\equiv \frac{1}{\epsilon - \epsilon_{\mathbf{k}} + i(\Gamma^L + \Gamma^R)/2}, \\ \rho_0 &= -\frac{1}{\pi} \sum_{\mathbf{k}\sigma} \mathrm{Im}[G^0_{\mathbf{k}\sigma\mathbf{k}\sigma}], \quad (6) \\ F(i\omega) &\equiv -\sum_{\mathbf{q}\nu} |V_{\mathbf{q}}|^2 \int d\tau e^{i\omega\tau} \\ &\langle T_\tau [a^\dagger_{\mathbf{q}}(\tau) + a_{\mathbf{q}}(\tau)] d_\nu(\tau) [a^\dagger_{\mathbf{q}}(0) + a_{\mathbf{q}}(0)] d^\dagger_\nu(0) \rangle. \quad (7) \end{aligned}$$

By assuming that the locations of the Kondo atoms $\mathbf{r}_i$ are completely random, we can reduce the double momentum sum into a single sum. The result for the differential conductance is proportional to

$$\sum_{\mathbf{k}\sigma\mathbf{k}'\sigma'} \mathrm{Im}[G^r_{\mathbf{k}\sigma\mathbf{k}'\sigma'}(\epsilon)] \simeq -\pi\rho_0 \left(1 + \frac{n}{\rho_0 D} \frac{\rho_0}{\pi} \mathrm{Im}[F(\epsilon)] \right), \tag{8}$$

where D and $-D$ are set to be the cut-off energies above and below the Fermi level. On the right hand side of Eq. (8), since ρ_0 gives the information on the number of conducting channels of the bare nanowire, the additional term in the parenthesis is the change caused by the Kondo atoms. The part of $\rho_0 \mathrm{Im}[F(\epsilon)]$ is the effect contributed by one single atom. The factor $n/\rho_0 D$ is an interference parameter due to the random locations of the Kondo atoms. This factor is basically determined by the surface-to-volume ratio since n is the number of atoms on the surface and $\rho_0 D$ gives the total number of states on the wire. The surface-to-volume ratio here also contributes to the average coupling constants V and V_0 because the surface states couple more strongly to the atoms on the surface.

To evaluate the correlation function in Eq. (7), we adapt the $1/N$ expansion with the approximation of $U \to \infty$[15] to solve the photon-assisted Anderson model.

To demonstrate the feasibility, it is sufficient to stop at the second order perturbation theory and keep only $(1/N)^0$ terms. The lowest non-trivial order Feynman diagram plotted in Fig. 2 and the calculation of Eq. (7) follows the procedures in Ref.[15].

Since $k_BT \ll \hbar\omega_{\rm SPR}$, only the surface plasmon states at the incident laser frequency are populated, and like its laser source, is in a coherent state $|\alpha_{\mathbf{q}}\rangle\delta_{\omega_{\mathbf{q}},\omega_l}$. Also it is natural to assume that the laser frequency $\omega_l = \omega_{\rm SPR}$ and the surface plasmon states have no degeneracy at the laser frequency, so that $|\alpha_{\mathbf{q}}\rangle\delta_{\omega_{\mathbf{q}},\omega_l} = |\alpha_l\rangle$. The self energy correction at zero temperature to the right part of the diagram in Fig. 2 is

$$\Sigma_0(z) = \frac{N_d\Delta_0}{\pi}\ln\left|\frac{z-\epsilon_d}{z-\epsilon_d-D}\right| + \frac{\alpha_l^2 N_d\Delta}{\pi} \cdot\left[\ln\left|\frac{z-\epsilon_d-\omega_l}{z-\epsilon_d-D-\omega_l}\right| + \ln\left|\frac{z-\epsilon_d+\omega_l}{z-\epsilon_d-D+\omega_l}\right|\right] + \frac{N_d\Delta}{\pi} \cdot\sum_{\mathbf{q}}\frac{(\kappa/2)^2}{(\omega_{\mathbf{q}}-\omega_{\rm SPR})^2+(\kappa/2)^2}\ln\left|\frac{z-\epsilon_d-\omega_{\mathbf{q}}}{z-\epsilon_d-D-\omega_{\mathbf{q}}}\right|, \quad (9)$$

where $\Delta_0 \equiv \pi\rho_0 V_0^2$, $\Delta \equiv \pi\rho_0 V^2$. The first term on the right-hand side of Eq. (9) is the self energy as in the original Anderson Model. The second term corresponds to the electron hopping with stimulated surface plasmon emission and absorption. The last term is the electron hopping while spontaneously emitting a surface plasmon. The difference between the result of the original Anderson model and Eq. (9) is that there are two relevant branch cuts here. The branch cuts and the graphical solution for finding the poles are plotted in Fig. 3. Assuming $D \gg \epsilon_d, \omega_l$, there are two poles corresponding to the processes of electron tunneling with absorbing a surface plasmon and without a surface plasmon. The case of the dashed curve in Fig. 3 happens when the amplitude of the incident laser is too large. Under this circumstances, the Kondo effect is destroyed.

In the regime where the Kondo effect exists, the corresponding spectral function can be obtained by analytic continuation. The result for $T=0$ with the assumption of $\omega_l \gg \alpha_l^2 N_d\Delta, N_d\Delta_0$ is

$$\begin{aligned}\rho_0{\rm Im}[F(\epsilon)] \simeq -N_d\Bigg[&\Delta_0\left|1+\frac{N_d\Delta_0}{\pi\delta_0}\right|^{-1}\delta(\epsilon-\delta_0)\\ &+\alpha_l^2\Delta\left|1-\frac{\alpha_l^2 N_d\Delta}{\pi\delta_A}\right|^{-1}\delta(\epsilon+\delta_A)\\ &+\alpha_l^2\Delta\left|1+\frac{N_d\Delta_0}{\pi\delta_A}\right|^{-1}[\delta(\epsilon-\omega_l-\delta_0)+\delta(\epsilon+\omega_l-\delta_0)]\\ &+\Delta_0\left|1-\frac{\alpha_l^2 N_d\Delta}{\pi\delta_A}\right|^{-1}\delta(\epsilon-\omega_l+\delta_A)\\ &+\alpha_l^2\Delta\left|1-\frac{\alpha_l^2 N_d\Delta}{\pi\delta_A}\right|^{-1}\delta(\epsilon-2\omega_l+\delta_A)\Bigg]. \quad (10)\end{aligned}$$

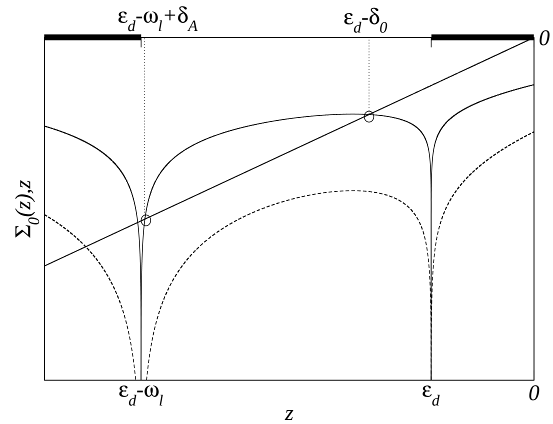

FIG. 3: Schematic graphical solution for the poles with the self energy of Eq. (9), $z = \Sigma_0(z)$. The solid curve and the dashed curve are the $\Sigma_0(z)$ for two different sets of parameters. For the solid curve, in addition to the original pole at $z = \epsilon_d - \delta_0$, another pole at $z = \epsilon_d - \omega_l + \delta_A$ appears corresponding to the process of electron hopping while absorbing a surface plasmon. The branch cuts, depicted as bold lines on the top, are chosen to be at $z < \epsilon_d - \omega_l$ and $\epsilon_d < z < \epsilon_d + \omega_l$, so that when the laser intensity $\alpha_l^2 \to 0$ the system goes back to the original Anderson model. For the dashed curve, there is no pole lying outside the branch cuts, hence no Kondo resonance.

In the measurement of nanowire differential conductance, the Kondo effect reveals itself as anti-resonances, which corresponds to the case with Fano parameter $q \to 0$[16, 17]. In the presence of the strong surface plasmon field, the Kondo peak near the Fermi surface splits into two due to the new opening of the surface plasmon assisted tunneling. The side bands near $\pm\omega_l$ and $2\omega_l$ also appear. The sizes of these anti-resonance peaks can be controlled by varying the incident laser intensity[18]. The reduction of the conductance at the antiresonances is due to the electrons at these energies have a resonant binding with the individual Kondo atoms and are unable to conduct electricity.

To estimate the feasibility, an *ab initio* calculation is carried out to estimate the parameters. Our *ab initio* calculation of the electronic structures of Co atoms interacting with the Au surface and the *sp*-*d* coupling strength caused by the $\mathbf{j}\cdot\mathbf{A}$ term is based on the full potential linear augmented Slater-type orbital (LASTO) method developed by Davenport and coworkers[19, 20, 21]. The LSDA+U scheme as described in Ref. [22] is adopted. It is believed that the LSDA+U method is more reliable than the LSDA method in determining the magnetization of strongly correlated systems. To study the *sp*-*d* hybridization between the Co adatom and the Au surface, we adopt a "supercell" model which contains five layers of Au on an fcc lattice (normal to the (111) direction) and three more vacuum layers. One Co adatom is placed on the (111) surface of the Au slab in each

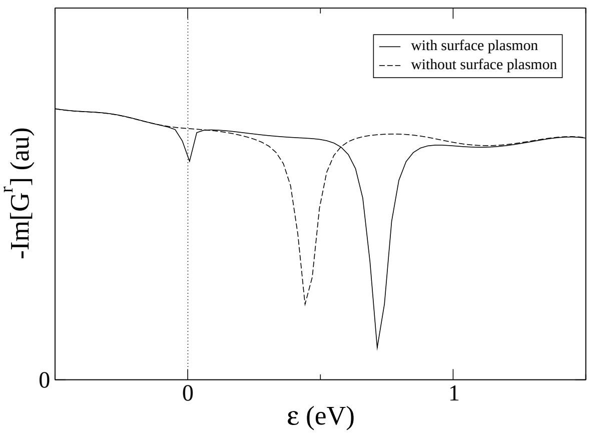

FIG. 4: The imaginary part of the retarded Green's function in Eq. (4) and Eq. (5). The delta functions in Eq. (10) are artificially replaced by broadened Loretzian functions of equal weight. The dashed curve shows the result of the Co atoms adsorbed on gold nanowire, and the solid curve shows that when the additional surface plasmon field is applied. It can be clearly seen that the presence of the strong and high frequency ($\omega_l > |\epsilon_d|$) EM field significantly shifts the original Kondo peak to the right and an extra peak below the Fermi level appears.

$\sqrt{3} \times \sqrt{3}$ surface unit cell (at equal distances from the three Au atoms underneath). The surface-to-volume ratio in this model is 1/5, so it corresponds to a nanowire of radius 10 atomic layers or a diameter of $10nm$ with 1/3 monolyer Co coverage on the surface. The on-site effective Coulomb repulsion is taken to be $U \sim 2.8$eV[23]. Our LSDA+U calculation shows that the averaged occupancy of the Co d orbitals is 7.92 (or a spin polarization of 2.08 μ_B). With this occupancy, we obtain $\epsilon_d \sim -1.18$eV, $\Delta_0 \sim 0.4$eV following the method used in Ref. [23]. Assuming the incident laser of 525nm wavelength has the focused intensity of 10^{11}W/cm^2, whose intensity of EM field is amplified by the surface plasmon resonance by 10^3, the resulting parameters $\alpha_l^2 \Delta \sim 0.2$eV, $\delta_A \sim 2$meV, and $\delta_0 \sim 0.72$eV. The dI/dV curve is shown in Fig. 4.

With the STM technology, the atoms on the wire can be arranged into any desired pattern. Then this design can be used to investigate the transport properties of 1D or 2D periodic Anderson model, since the nanowire can be readily replaced by a thin film. The periodicity of the Kondo atoms can be chosen at will, and the coupling parameters of surface plasmon assisted tunneling can also be tuned by simply varying the incident laser intensity. If realized, this could bring the problem of traditionally microscopic strongly correlated electron systems onto the surface of a mesoscopic scale.

In summary, we have proposed an experiment to measure the surface plasmon assisted Kondo effect of magnetic atoms adsorbed on a metallic nanowire and modeled the anticipated dI/dV curve via an *ab initio* calculation. Due to the good surface-to-volume ratio the electrons going through the nanowire are forced to scatter with the Kondo atoms, which in our numerical calculation on a Co/Au case gives a clearly observable effect. In addition, the introduction of localized surface plasmon field on the metallic nanowire adds new channels to the *sp*-*d* hybridization so that the electrons now can hop on and off the Kondo atom with absorbing or emitting real photons, which results in multiple Kondo peaks.

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